

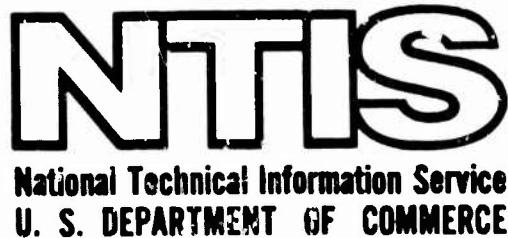
AD-783 496

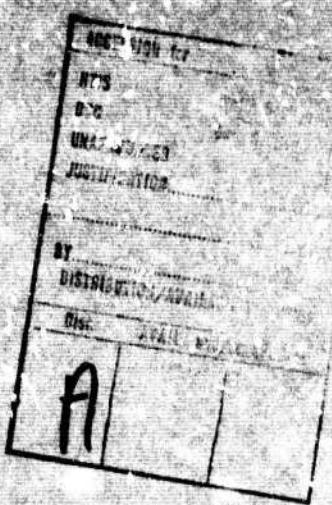
POLYAMIDES AND POLYSULFONAMIDES
FROM HEXAHYDROBENZO-DIPYRROLE

ARMY NATICK LABORATORIES

APRIL 1974

DISTRIBUTED BY:





Approved for public release; distribution unlimited.

Citation of trade names in this report does not constitute an official endorsement or approval of the use of such items.

Destroy this report when no longer needed. Do not return it to the originator.

ic

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AD 783 496

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 74-32-CE	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Polyamides and Polysulfonamides from Hexahydrobenzo-dipyrroie		5. TYPE OF REPORT & PERIOD COVERED Technical Report
7. AUTHOR(s) Namassivaya Doddi		6. PERFORMING ORG. REPORT NUMBER C&PLSEL-122
9. PERFORMING ORGANIZATION NAME AND ADDRESS US Army Natick Laboratories Kansas Street Natick, Massachusetts 01760		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62105A. IT062105A329, 02-113.
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE April 1974
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 26
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary, and identify by block number) See reverse side.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See reverse side.		

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

19. KEY WORDS:	Link A Role:	Link B Role:
Polymerization	8	
Fibers	9	
Protective Clothing	9	
Armored Vehicles	4	
Flight Crews	4	
Heat	4	
Flame	4	
Condensation Polymerization		8
Polyamides		9
Chlorides		9
Polymers		9
Calorimetry		10
Heat Measurement		10
Differential Thermal Analysis		10
Molecular Weight		4
Viscosity		1
Stabilization		4
20. <u>Abstract</u> - A series of polyamides was synthesized by the interfacial polycondensation of 1,2,3,5,6,7-hexahydrobenzo(1,2-c:4,5-c')dipyrrole with iso-phthalic, terephthalic, oxydibenzoic, sebasic and adipic acid chlorides. High molecular weight polymers with inherent viscosities ranging from 0.4 to 3.6 dl ⁻¹ were obtained. Polymerization with isophthaloyl chloride gave the highest molecular weight polymer in this series. These polyamides melt between 350°C and 475°C depending on structural differences as determined by differential scanning calorimetry. Rapid weight loss in these polymers was observed in the range of 350 - 400°C under thermogravimetric analysis in a nitrogen atmosphere. All these polyamides are susceptible to photo-oxidative degradation. The results were compared with Nomex polymer, poly(1,3-phenyleneisophthalamide).		
In addition, polysulfonamides were also prepared from hexahydrobenzo-dipyrrole with m-benzene, biphenyl and p,p'-oxydibenzene sulfonyl chloride by interfacial polycondensation and by solution polycondensation with (p,p'-oxydibenzene sulfonyl chloride). The polysulfonamides are considerably lower molecular weight and are less stable than the corresponding polyamides.		

10

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Approved for public release;
distribution unlimited

AD _____

TECHNICAL REPORT
74-32-CE

POLYAMIDES AND POLYSULFONAMIDES
FROM
HEXAHYDROBENZO-DIPYRROLE

by

Namassivaya Doddi

Series: CAPSEL-122

April 1974

Clothing and Personal Life Support Equipment Laboratory
U. S. ARMY MATTER LABORATORIES
Matick, Massachusetts 01760

ib

FOREWORD

This research was accomplished while the author held a National Research Council Resident Research Associateship at the US Army Natick Laboratories. The author wishes to express his appreciation to Dr. John H. Cornell and Mr. John T. Stapler for many helpful suggestions.

TABLE OF CONTENTS

	<u>Page</u>
List of Tables	iv
List of Figures	v
I. INTRODUCTION	1
II. EXPERIMENTAL	3
A. Monomer Preparation	3
B. Polymerizations	3
C. Viscosity Measurements	4
D. Thermal Analysis	4
III. RESULTS AND DISCUSSION	4
Polyamides	4
(1) Polymer Preparation	4
(2) Thermal Analysis	5
(3) Photo-oxidative Degradation	7
(4) Proposed Stabilization	8
(5) Conclusions	8
IV. POLYSULFONAMIDES	8
A. Preparation of Polymers	8
B. Thermal Properties	9
V. REFERENCES	26

LIST OF TABLES

	<u>Page</u>
I. Polyamide Repeat Units and their Identifying Names	11
II. Polysulfonamide Repeat Units and their Identifying Names	12
III. DSC-Melt Transition and Decomposition Temperatures	13
IV. Summary of Results on Synthesis of Polyamides from Di-isoindoline Dihydrobromide	14
V. Change in Inherent Viscosities with Time of Various Polyamides	15
VI. Change in 150°C Transition for PDIPA-4 with Time	16
VII. Summary of Results on Synthesis of Poly(Di-isoindoline Sulfonamides)	17
VIII. Thermal Analysis of Polysulfonamides	18

LIST OF FIGURES

	<u>Page</u>
1. DSC - Thermograms of Various Polyamides from Di-isoindoline	19
2. Thermogravimetric Analysis of Polyamides	20
3. Comparison of Thermogravimetric Analysis of Various High-Temperature Polyamides	21
4. Thermogravimetric Analysis of PDIPA-4: (A) Initial, (B) After 12 Days	22
5. DSC Thermograms of DIPA-4: Measured (A) the Day After Polymerization; (B) After 6 days; (C) After 27 days	23
6. IR-Spectra of PDIPA Film. (____) 0 hr., (----) 42 hr., Unfiltered Mercury Arc Irradiation in Air	24
7. Thermogravimetric Analysis of Polysulfonamides	25

POLYAMIDES AND POLYSULFONAMIDES FROM HEXAHYDROBENZO-D₇ PYRROLE

I. INTRODUCTION

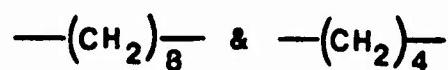
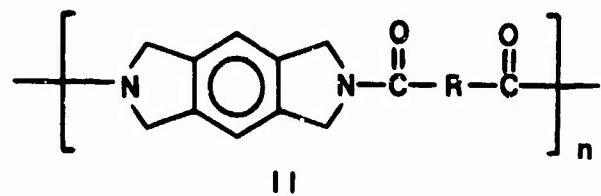
The US Army has a large number of applications for high temperature resistant fibers derived from organic polymers. One of the most important is to provide protective clothing for armored vehicle and air crewmen who may be exposed to intense heat and flame. The only commercially available material currently used is a wholly aromatic polyamide (Nomex), produced by the duPont Company.^(1,2) This material is only capable of partially meeting the Army requirements.

The continued demand for high temperature resistant fibers has stimulated an intensive search for new thermally stable polyamides and wholly aromatic heterocyclic polymers. The chemistry and thermal stability of some of these polymers has been summarized by Wallenberger.⁽³⁾ More recent progress through the efforts of both the Monsanto and duPont Companies in the production of experimental high temperature and high modulus fibers is discussed by Bleck and Preston.⁽⁴⁾

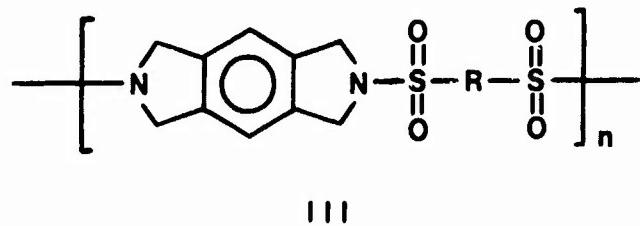
A new cyclic secondary diamine, 1,2,3,5,6,7-hexahydrobenzo(1,2-c:4,5-c')dipyrrole, or di-isoindoline (I), was initially synthesized by Stapler and Bornstein.⁽⁵⁾ It was interesting to use this new diamine as a starting material for high temperature polyamides and polysulfonamides because of its unique combination of structural features.



The present investigation was undertaken to study the preparation of a new class of polyamides (II) from the dihydrobromide of di-isoindoline (I) by interfacial polycondensation⁽⁶⁾ with five different diacid chlorides.



The structural formulas for the polyamide backbone repeat unit are given in Table I together with their identifying names. In addition, polysulfonamides (III) were also prepared by both interfacial and solution polycondensation with three different aromatic disulfonyl chlorides.



The polysulfonamide repeat units and their identifying names are summarized in Table II.

Thermal characterization of both polyamides and polysulfonamides was accomplished by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results of these characterizations are summarized and the thermal properties of di-isoindoline polyamides compared with data on Nomex polymer, poly(1,3-phenylene isophthalamide) obtained under the same conditions in Table III.

II. EXPERIMENTAL

A. Monomer Preparation

The dihydrobromide of the monomer, 1,2,3,5,6,7-hexahydrobenzo-(1,2-c:4,5-c')dipyrrole was synthesized by the procedure of Stapler and Bornstein.⁽⁵⁾ The diacid chlorides isophthaloyl, terephthaloyl, sebacyl and adipyl chlorides were commercially obtained and purified according to the procedures described elsewhere.⁽¹²⁾ The 4,4'-oxydibenzoyl chloride was synthesized by the reaction of dicarboxy diphenyl ether with thionyl chloride. The product was recrystallized three times from benzene and characterized by elemental analysis and IR spectra.

Metabenzene and 4,4'-biphenyldisulfonyl chlorides were obtained from Aldrich Chemical Company and they were recrystallized from benzene solution. The 4,4'-oxydibenzenesulfonyl chloride was obtained from the Research Organic/Inorganic Chemical Company and it was recrystallized from dry benzene solution.

B. Polymerizations

A typical interfacial polymerization was carried out as follows: a 200-ml Bantam Ware 4-neck resin kettle was fitted with stirrer, two 25-ml addition funnels and a nitrogen bleed. Into the kettle were placed 0.9660 g. (0.003 mole) di-isoindoline dihydrobromide and 35 ml distilled water while the system was vigorously stirred. A solution of sodium hydroxide 0.4800 g. (0.012 mole) in 10-ml water was placed in one addition funnel and in the other was placed a solution of isophthaloyl chloride 0.6090 g. (0.003 mole) in 15-ml of dry methylene chloride. While the aqueous phase was vigorously stirred, the solutions of sodium hydroxide and the acid chloride were simultaneously added over a period of 30 seconds. The polymer instantly precipitated out as a white swollen solid. The mixture was then stirred for a period of 15 minutes and the methylene chloride was evaporated on a steam bath. The resulting polymer was filtered and washed several times with hot water, cold water, alcohol and finally with acetone. It was dried under vacuum at 60°C overnight. The yield calculated on the basis of the molecular weight of the repeat unit was 90 percent.

The polysulfonamides were also prepared by interfacial polycondensation according to the above procedure.

A typical interfacial polymerization in Waring Blender was carried out as follows: in a 1-qt. Waring home blender was placed a solution of 3.268 g. (0.0101 mole) of di-isoindoline dihydrobromide in 100-ml of water. The blender jar cover was equipped with two addition funnels. A solution of sodium hydroxide 1.770 g. (0.0442 mole) in 30-ml water was placed in one addition funnel and in the other was placed a solution of isophthaloyl chloride 2.185 g. (0.0107 mole) in 35-ml dry methylene chloride. The blender speed was turned to medium speed and there were added the solutions of sodium hydroxide and the acid chloride over a period of 30 seconds. After the mixture had been stirred for 15 minutes, methylene chloride was evaporated and the polymer was collected on a fritted glass filter and washed with water until free of alkali and then with acetone. The granular polymer was dried in a vacuum oven at 50°C. The yield was 90%.

C. Viscosity Measurements

Inherent viscosities ($\ln \eta_{sp}/C$) of polyamides were determined in water-white redistilled m-cresol at 30°C and a concentration (C) of 0.5 g. in 100 ml of solution. The inherent viscosities of polysulfonamides were determined in concentrated (95%) sulfuric acid.

D. Thermal Analysis

A duPont 990 differential scanning calorimeter (DSC) was used to determine the thermal transitions. Thermogravimetric analysis was performed in a Perkin Elmer (TGS-1) thermobalance. All measurements were with nitrogen sweep. Temperature corresponding to the onset of rapid weight loss is taken as the decomposition temperature. A Hanovia 550-watt high pressure mercury arc lamp was used to expose PDIPIA film in air. GPC analysis was carried out on a Waters instrument at 95°C in m-cresol using a series of four 10^6 Å^2 columns.

III. RESULTS AND DISCUSSION

Polyamides

(1) Polymer Preparation

A series of polyamides was prepared from di-isoindoline dihydrobromide using five selected diacid chlorides. The interfacial method was employed in which methylene chloride was used as the organic phase. All polymerizations were carried out at room temperature for a 15-minute period with the exception of PDSA which was prepared at 5°C for the same time. Equal mole ratios of the reactants were employed except for those cases where it is noted and aqueous sodium hydroxide was used as the acid acceptor. The results of polymer synthesis are summarized in Table IV.

Polymers of higher inherent viscosity were obtained from isophthaloyl chloride than from the other acid chlorides. Differences in inherent viscosities of magnitude shown in column 1 of Table IV probably

indicate higher molecular weight for the polyisophthalamides. Several factors, such as solvent effects, temperature, stirring and concentration effects, acid acceptor, dispersing agent, hydrolysis of acid chlorides, etc., influence the yields and molecular weights of polymers prepared by interfacial method.⁽⁶⁾ It was not the object of this investigation to study these factors in detail. However, the influence of the stirring speed could be seen in the case of PDIPA-4 which was prepared in a Waring blender at very high speed. The other polymers were prepared in a resin kettle equipped with regular laboratory mixer. Lower molecular weights and lower yields were obtained with terephthaloyl and adipyl chlorides. Decreasing temperature of reaction in the case of PDSA-4 had negligible effect.

Finally, PDIPA-5 polymer with an inherent viscosity of 3.6 was prepared using a fresh batch of recrystallized isophthaloyl chloride in a Waring blender at high speed. This is the highest molecular weight polymer obtained in this series and it may be attributed to the purity of the acid chloride.

The IR spectra of all of the polyamides had strong absorption at 1640 - 1620 cm^{-1} corresponding to the amide carbonyl linkages. The GPC analysis of polymers PDIPA-3 and PDSA-1 showed a broad log normal molecular weight distribution with polydispersity indices of 3.2 and 3.4 respectively. The distribution in PDODBA-3, however, was much broader (index 5.7) and bipopulate.

All the polymers prepared were initially white and separated from the reaction as powders or in fibrous form. They were found to be completely soluble in hexafluoroisopropanol (HFIP), m-cresol, and partially soluble in boiling chloroform. However, on long standing, all the polymers turned yellow, after which they swelled in hexafluoroisopropanol but did not dissolve. This behavior will be further discussed later.

High molecular weight polymers (FDIPA, PDODBA and PDSA) could be cast into tough films from hexafluoroisopropanol and m-cresol. Fibers could also be drawn from a test tube from concentrated solution in HFIP. Further investigation of fiber-forming capabilities and their properties will have to wait until larger quantities of these polymers are made.

(2) Thermal Analysis

Thermal transitions in all the polymers were investigated by differential scanning calorimetry from -80°C to 500°C and their thermal stability was studied by thermogravimetric analysis (TGA) in nitrogen. Below 0°C no transitions were observed. A gradual deviation of the DSC base line at 10-20°C (Figure 1) and an endothermic peak around 100°C is attributed to the desorption of water. Absence of 0°C melt transition and

the extent of endothermic transition in this desorption process indicate that the water molecules may be tightly bound to the polymer chain by hydrogen bonding between carbonyl groups. The mechanism of water sorption in polyamides was discussed in detail by Puffr and Sebenda⁽⁷⁾ and more recently for wet nylon-6 by Kapur et al.⁽⁸⁾ An exothermic transition (Figure 1) with a peak maximum between 150-175°C was observed following the water desorption endotherm in all the polyamides. However, when the same sample was quench-cooled from 200°C and reheated, this transition disappeared, nor was it observed when DSC measurements were made on freshly prepared samples. This behavior will be discussed later.

The DSC melt temperatures and the decomposition temperatures from TGA for various polymers are summarized in Table III. The thermograms of the polyamides show endothermic peaks (Figure 1) between 350°C and 475°C depending on structural differences. Whether these endotherms can be legitimately regarded as the melt transitions is debatable in the light of the fact that thermogravimetric analysis curves (Figure 2) showed 20-30% weight loss by the time temperatures reached the peak values. This behavior is indicative of a rather severe susceptibility to oxidative and thermal degradation below the melt temperature. These polymers did not melt in the conventional sense and similar behaviors have been reported for additional polyamide systems by Preston and Black.^(9,10) Above the peak value temperature, the polymer samples appeared to be carbonized to a black cake. The PDTPA has the best thermal stability in this family of polyamides even though its molecular weight was relatively low. It is also seen that Nomex polymer has a higher melting transition and higher decomposition temperature than the materials under discussion in this paper.

Based on the data for PDIPA and PDTPA it appears that the presence of the paraphenylene moiety in PDTPA increased the melting point and the decomposition temperature. As expected, the presence of an ether linkage in PDODBA accounts for a lower melting temperature and increased susceptibility to thermal and oxidative degradation relative to PDTPA. Aliphatic derivatives PDSA and PDAA (Figure 2) undergo rapid decomposition at lower temperatures, 300-350°C due to the lack of thermal stability of the aliphatic linkages compared to their aromatic counterparts. No clear indication of glass transition temperatures was observed in the DSC thermograms.

The thermal stability of the most promising member of the diisoindoline polyamides, PDIPA, is compared with other materials under investigation at the US Army Natick Laboratories. The materials investigated are Nomex polymer, Nomex twill, Nomex 2 and Kevlar (Fiber B) and the TGA results are summarized in Figure 3. The thermal stability of PDIPA, soon after it has been prepared, is comparable to Nomex polymer. However, it decreased with time as discussed in the following section. Best thermal stability is observed in the case of Kevlar (Fiber B) made by the duPont Company. Even at temperatures as high as 580°C it shows only a 10 percent

loss in weight. The second best is Nomex 2 material with a 10 percent loss of weight at 510°C.

3. Photo-oxidative Degradation

It is observed that all the polyamides derived from di-isoindoline are susceptible to photo-oxidative degradation both in solid state or in solution. After long standing in the solid state under laboratory conditions, the inherent viscosity in m-cresol of all the polymers was drastically reduced. Contrary to expectation, the photo-degraded polymers were no longer soluble in hexafluoroisopropanol despite the decrease in molecular weight indicated by the lowered viscosity. These results may be due to polymer oxidation initiated photochemically by ambient light. The changes in inherent viscosities with time for various polymers are summarized in Table V.

Figure 4 records the change in thermal stability, revealing a 20-30°C lower decomposition temperature. The melt transition is lowered by 40°. It is also seen that this change was more drastic in PDIPA-4 than others. This is probably due to the fine particle size of this sample which resulted in greater surface exposure to light and oxygen.

While the inherent viscosity decreased with time, an increase in magnitude of the exothermic transition around 150°C discussed earlier was observed. It was followed closely in PDIPA-4 sample. The results are summarized in Table VI and the changes in exothermic transitions are shown in Figure 5. Initially, the day after the polymer was made, the 150° transition did not appear, but after 6 days an exothermic peak (curve B) with a peak area of 0.3500 in.²/mg. of sample was observed. Another sample from the same batch of the polymer after 27 days gave an exotherm (curve C) with a considerable increase in peak area (Table V).

A preliminary investigation of the effect of U.V. radiation on a tough, flexible PDIPA-4 film was carried out by following the changes in IR spectra after exposing it to U.V. radiation. It was observed that the amide I absorption band at 1640 cm⁻¹ gradually broadened and after 42 hours of exposure became a part of a wide absorption band at 1730-1720 cm⁻¹. At the same time there was an almost complete disappearance of the methylene group absorption at 2910 cm⁻¹ and 2853 cm⁻¹ as seen in Figure 6. The polymer film was initially clear and colorless, but after 42 hours of exposure to U.V. radiation, it turned dark yellow and became very brittle. It was also no longer soluble in hexafluoroisopropanol (HFIP). However, that portion of the film covered by the cardboard holder and not exposed to the radiation was soluble in HFIP.

All the above observations reflect the fact that these polyamides degraded as a result of photochemical initiation. The DSC exothermic transition may be associated with some further chemical

reaction. The photodegradation of commercial Nomex was studied by Carlson, Parnell and Wiles.⁽¹¹⁾ However, the effect of radiation from ordinary fluorescent light sources is far more severe in the case of di-isoindoline polyamides than Nomex polymer. This striking difference may be due to the allylic -CH₂ groups in di-isoindoline as evidenced by the disappearance of -CH₂ IR bands in the irradiated sample. The mechanism for this degradation process is not known at the present time and it is the subject of future investigation.

(4) Proposed Stabilization

Practical application of polyamides based on di-isoindoline will probably require development of methods to prevent their degradation under conditions of use. The stabilization of various polymers was discussed by Hawkins⁽¹³⁾ and more specifically U.V. stabilization of polyamides and polyamide fibers was summarized in Encyclopedia of Polymer Science.⁽¹⁴⁾ An investigation has been made by Kransky and Schwartz⁽¹⁵⁾ of several systems to improve the resistance of Nomex to actinic degradation. Some of the organic U.V. inhibitors studied by them were p-dimethylaminoazobenzene, acetone 2,4-dinitrophenylhydrazone, p-nitroaniline and p-phenylazoaniline. The effect of these and some other U.V. absorbers on di-isoindoline polyamides should be studied before attempting to spin fibers out of these polyamides.

(5) Conclusions

High molecular weight polyamides can be prepared from di-isoindoline by the interfacial polycondensation with various diacid chlorides. The highest molecular weight polymer was obtained with iso-phthaloyl chloride which was comparable in thermal stability to Nomex polymer, poly(1,3-phenylene isophthalamide). However, all these polyamides are susceptible to photo-oxidative degradation. Consequently, they should be stabilized before making fibers from them.

IV. POLYSULFONAMIDES

A. Preparation of Polymers

Polysulfonamides were prepared from di-isoindoline dihydrobromide by the interfacial polycondensation technique in an organic solvent-water system. The disulfonyl chlorides used were m-benzenedisulfonyl chloride, biphenyldisulfonyl chloride and 4,4'-oxy-bis(benzenesulfonyl chloride). In most cases methylene chloride was used as an organic phase and aqueous sodium hydroxide solution was employed as the acid acceptor. The results of polymer synthesis are summarized in Table VII. In all cases of interfacial polycondensation the polysulfonamides obtained were only soluble in concentrated sulfuric acid and exhibited low inherent viscosities in that solvent. Increased reaction time and higher reaction temperatures in the case of polycondensation with m-benzenedisulfonyl chloride had negligible

effect on the inherent viscosities. Therefore, these parameters were not studied in the case of the other two disulfonyl chlorides.

Preparation of completely aromatic polysulfonamides by solution polycondensation was reported by Arnold, Cantor, and Marvel.⁽¹⁶⁾ Poly-sulfonamides from piperazine were investigated by Evers and Whlers.⁽¹⁷⁾ In both the reports, polysulfonamides with only low inherent viscosity numbers were obtained. No high molecular weight completely aromatic polysulfonamides were reported.

The low molecular weights which were obtained with the di-iso-] indoline polysulfonamides may be due to the low reactivity of the secondary diamine with the aromatic disulfonyl chlorides and the hydrolysis of the disylfonyl chlorides in the presence of water.

In an attempt to prepare high molecular weight polysulfonamides from di-isoindoline by the solution method of polycondensation, methylene chloride was employed as solvent. However, the investigation was carried out only with *p,p'*-oxy-bis(benzenesulfonyl chloride) because of ready availability of pure recrystallized material. Polymers with higher inherent viscosities were obtained in almost quantitative yields by using two different inorganic acid acceptors. The polymerizations were carried out under nitrogen atmosphere in order to minimize the hydrolysis of disulfonyl chlorides by traces of moisture.

In general, all the polymers were white or cream colored powdery materials. Because of their limited solubility in concentrated sulfuric acid, molecular weight determinations could not be performed. The elemental analysis and infrared spectra of the polymers were fairly consistent with the proposed structures. In all cases, the IR spectra exhibited absorption bands at 1330 - 1350 cm⁻¹ and 1130 - 1160 cm⁻¹ indicative of sulfonamide group.

B. Thermal Properties

Differential thermal analysis of these polymers was carried out by DSC in the temperature range of 0 to 500°C. No indication of melting was observed. The thermograms revealed multiple exotherms between 300 and 400°C attributed to decomposition of the polymer. Above the peak value temperatures the polymer samples appeared to be carbonized. The thermal stability of these polysulfonamides was evaluated by thermogravimetric analysis and plots of percent weight loss versus temperature are shown in Figure 7. All these polymers show breakdown in the region of 280 - 310°C.

The rapid weight loss in the vicinity of 300°C in all cases is associated with evolution of sulfur dioxide as identified by IR. Poly samples were pyrolyzed at 350°C and the IR spectra of the gaseous prod were taken. Comparison of these spectra with a standard IR spectrum of sulfur dioxide⁽¹⁸⁾ confirmed the evolution of this gas upon decomposition of polysulfonamides.

A summary of thermal behavior of these polysulfonamides is given in Table VIII. As can be seen, these di-isoinoline polysulfonamides are of considerably lower molecular weight and are less stable than the di-isocindoline polyamides reported in an earlier section.

TABLE I

POLYAMIDE REPEAT UNITS
AND
THEIR IDENTIFYING NAMES

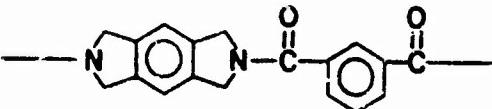
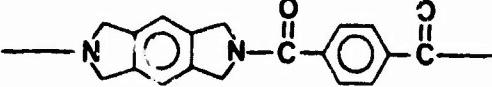
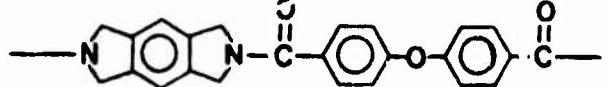
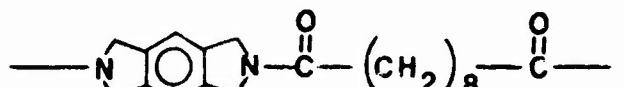
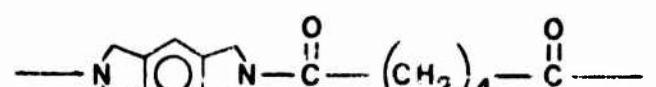
<u>Diacid Chloride</u>	<u>Polymer Structural Formula</u>	<u>Polymer Identification Name</u>
Isophthaloyl		PDIA
Terephthaloyl		PETPA
Oxy-DiBenzoyl		PDCDBA
Sebacoyl		PDSA
Adipyl		PDAA

TABLE II
POLYSULFONAMIDE REPEAT UNITS
AND
THEIR IDENTIFYING NAMES

<u>DISULFONYL CHLORIDE</u>	<u>POLYMER REPEAT UNIT</u>	<u>POLYMER IDENTIFICATION NAME</u>
m-Benzene		PDMBSA
Bi-Phenyl		PDBPSA
Oxy-Dibenzene- sulfonyl		PDODESA

TABLE III
DSC-MELT TRANSITION AND DECOMPOSITION TEMPERATURES

<u>POLYMER</u>	<u>MELT TRANSITION °C</u>		<u>DECOMPOSITION TEMP °C</u> (TGA)
	<u>Onset</u>	<u>Peak</u>	
PDIPA	380	415	360
PDTPA	435	475	405
PDODEA	380	400	390
PDSA	350	400	305
PDAA	420	455	350
NOMEX	400	425	430

TABLE IV
SUMMARY OF RESULTS ON SYNTHESIS OF POLYAMIDES
FROM DI-ISOINDOLINE DIHYDROBROMIDE

POLYMER	DIACID CHLORIDE Conc. M/l	DIHYDROBROMIDE Conc. M/l	γ_{inh}^*	YIELD Percent
PDIPA-1	0.22	0.10	1.50	90
PDIPA-3 ^a	0.17	0.10	1.52	90
PDIPA-4 ^a	0.21	0.10	2.30	92
PDIPA-5	0.30	0.10	3.6	90
PDTPA-1	0.10	0.10	0.40	82
PDTPA-1	0.20	0.10	0.34	80
FDODBA-2	0.30	0.10	0.79	99
PDODBA-3 ^a	0.10	0.10	0.73	99
PDSA-3	0.30	0.10	0.81	99
PDSA-1 _b	0.20	0.08	0.51	97
PDSA-4 _b	0.20	0.08	0.80	99
PDAA-1	0.26	0.10	0.33	54
PDAA-2	0.26 ^a	0.10	0.39	64

*Conc. 0.5g dl⁻¹ in m-cresol at 30°C

a - excess acid chloride is used

b - polymerized at 5°C

TABLE V

CHANGE IN INHERENT VISCOSITIES WITH TIME
OF VARIOUS POLYAMIDES

<u>POLYMER</u>	<u>INHERENT VISCOSITY*</u> (dl g ⁻¹ ; initial)	<u>TIME LAPSE</u> (in days)	<u>INHERENT VISCOSITY*</u> (dl g ⁻¹ after time lapse)
PDIPA-1	1.50	219	0.35
PDIPA-4	2.30	18	0.45
PDODBA-2	0.79	189	0.40
PDODBA-3	0.73	30	0.53
PDSA-4	0.83	237	0.40

*0.5g dl⁻¹ in m-cresol at 30°C

TABLE VI
CHANGE IN 150°C TRANSITION FOR PDIPA-4 WITH TIME

<u>DSC Traces</u>	<u>Weight, mg.</u>	<u>Time Lapse</u> <u>days</u>	<u>Area, Inch²</u>	<u>Area/Weight</u> <u>Inch²/Mg</u>
(a)	4.8	----	----	----
(b)	5.0	6	1.75	0.3500
(c)	6.1	27	4.47	0.7327

Based on DSC traces, Figure 5. Area obtained by integration of traces (a), (b), (c) respectively.

TABLE VII
SUMMARY OF RESULTS ON SYNTHESIS OF
POLY(DI-ISOINDOLINE SULFONAMIDES)

<u>Polymer</u>	<u>Reaction Time</u> Min.	<u>Reaction Solvent</u>	<u>Temperature</u> °C	η_{inh}^a dl/g	<u>Percent Yield</u>
PDMBSA-1	45	Benzene	55	0.15	97
PDMBSA-2	45	Xylene	80	0.18	95
PDMBSA-3	45	Benzene	23	0.17	99
PDMBSA-4	300	Toluene	23	0.16	96
PDBPSA-2	45	Methylene chloride	23	0.15	88
PDODBSA-1	20	Methylene chloride	23	0.18	97
PDOPBSA-S-1	45 ^b	Methylene chloride	23	0.50	99
PDODBSA-S-2	45 ^c	Methylene chloride	23	0.69	98

a - 0.5 g in 100 ml of concentrated H₂SO₄ at 30°C

b - Solution polymerization; calcium hydroxide as acid acceptor

c - Solution polymerization; sodium hydroxide as acid acceptor

TABLE VIII
THERMAL ANALYSIS OF POLYSULFONAMIDES

<u>Polymer</u>	<u>TGA Decomposition Temperature °C</u>	<u>DSC Decomposition Exothermic Transition Onset Peak °C</u>
PDMBSA	300	300 332
PDBPSA	295	250 310
PDODBSA	285	230 300
PDODBSA-S*	308	300 325

*Solution polymerized; inherent viscosity 0.69 dl_g⁻¹

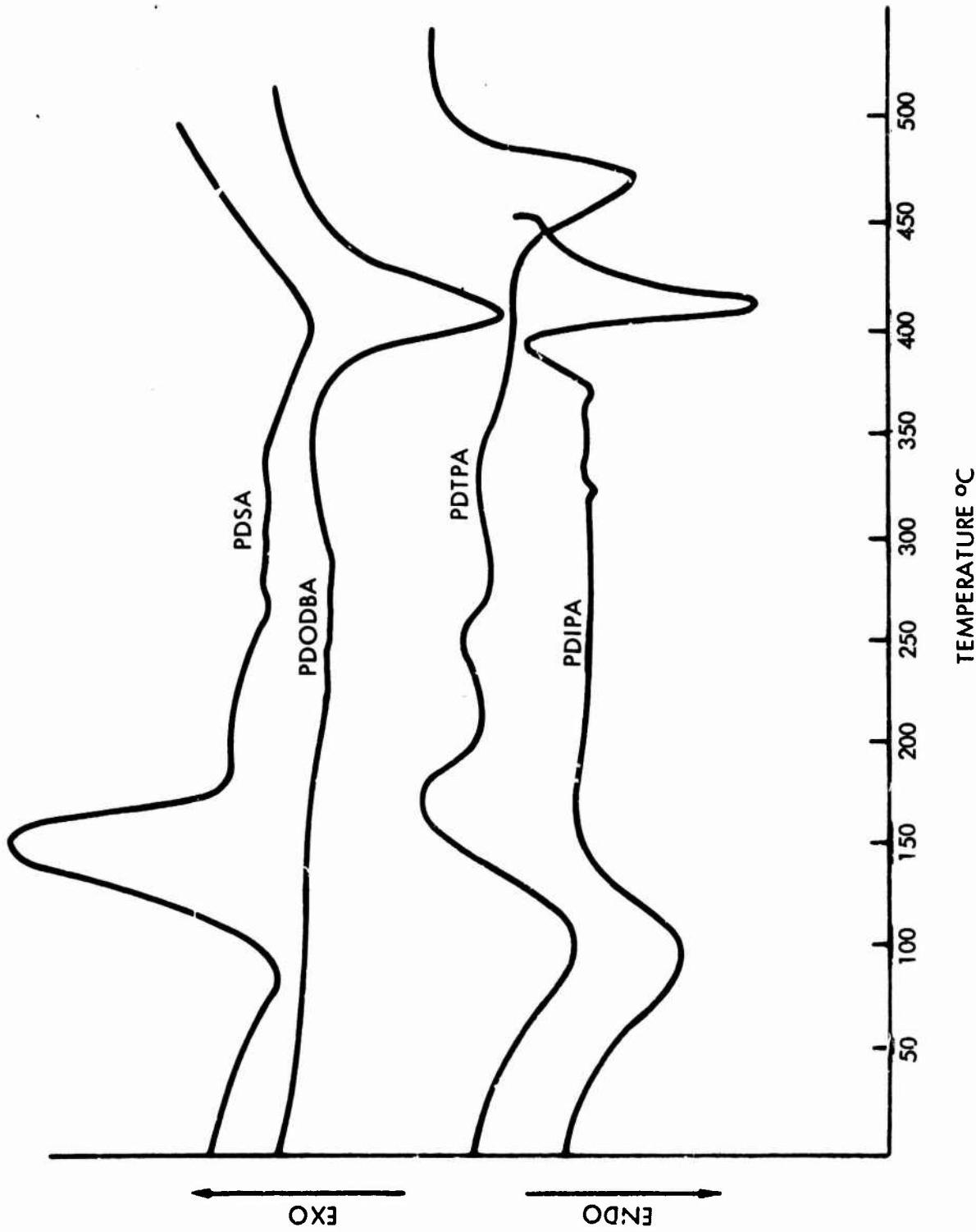


Figure 1. DSC - Thermograms of Various Polyamides from Di-isooindoline

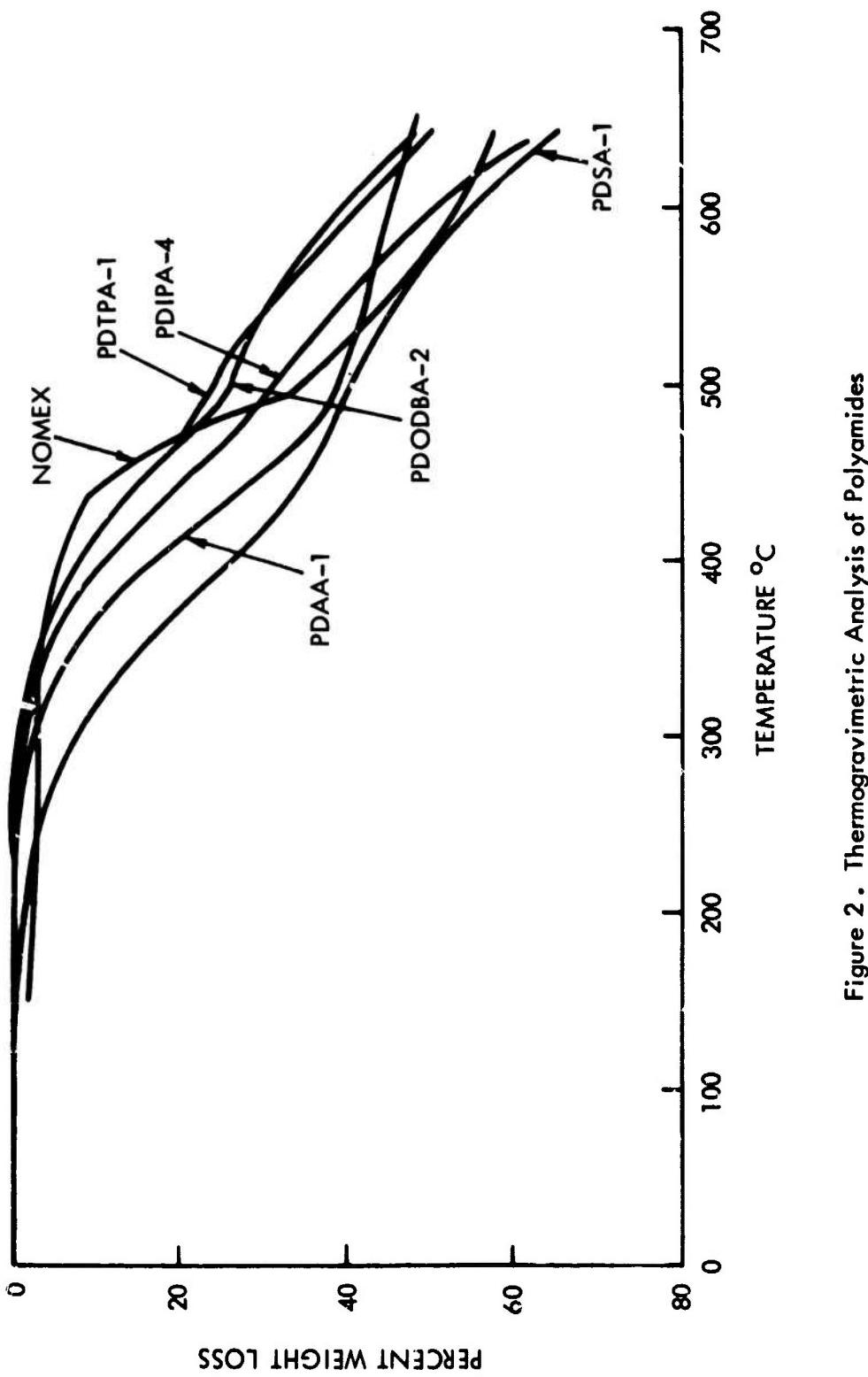


Figure 2. Thermogravimetric Analysis of Polyamides

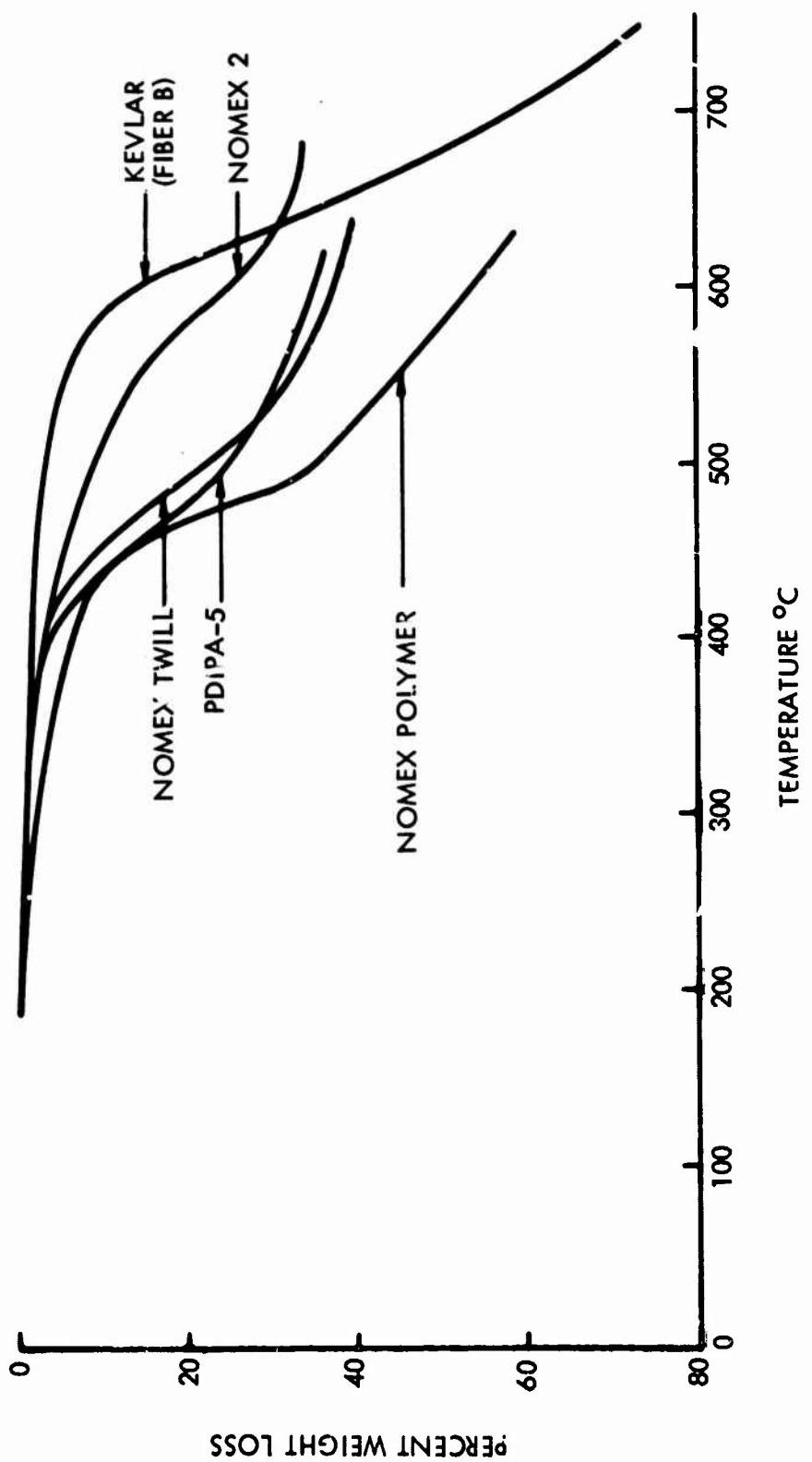


Figure 3. Comparison of Thermogravimetric Analysis of Various High-Temperature Polyamides

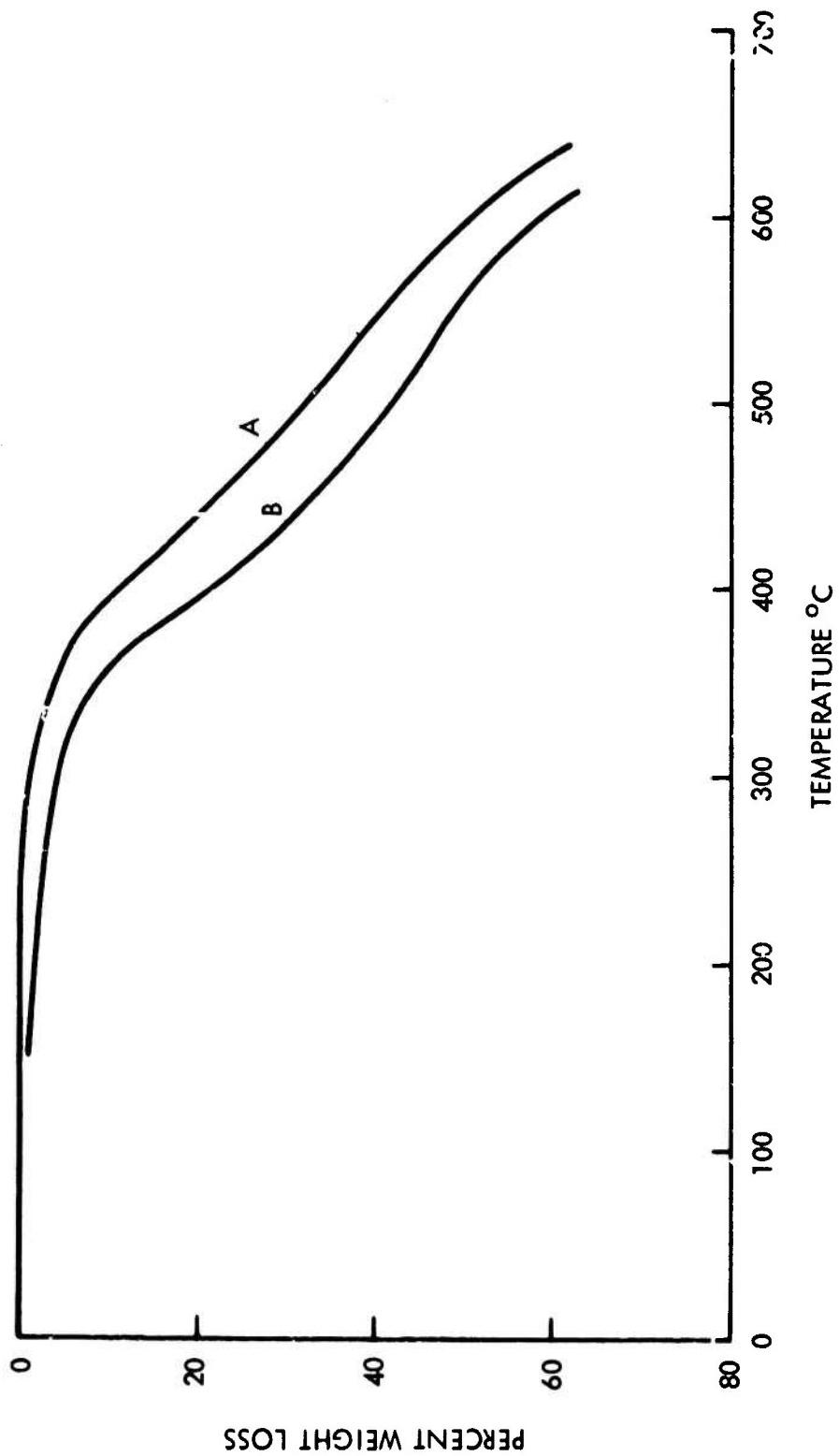


Figure 4. Thermogravimetric Analysis of PDIPA-4: (A) Initial, (B) After 12 Days

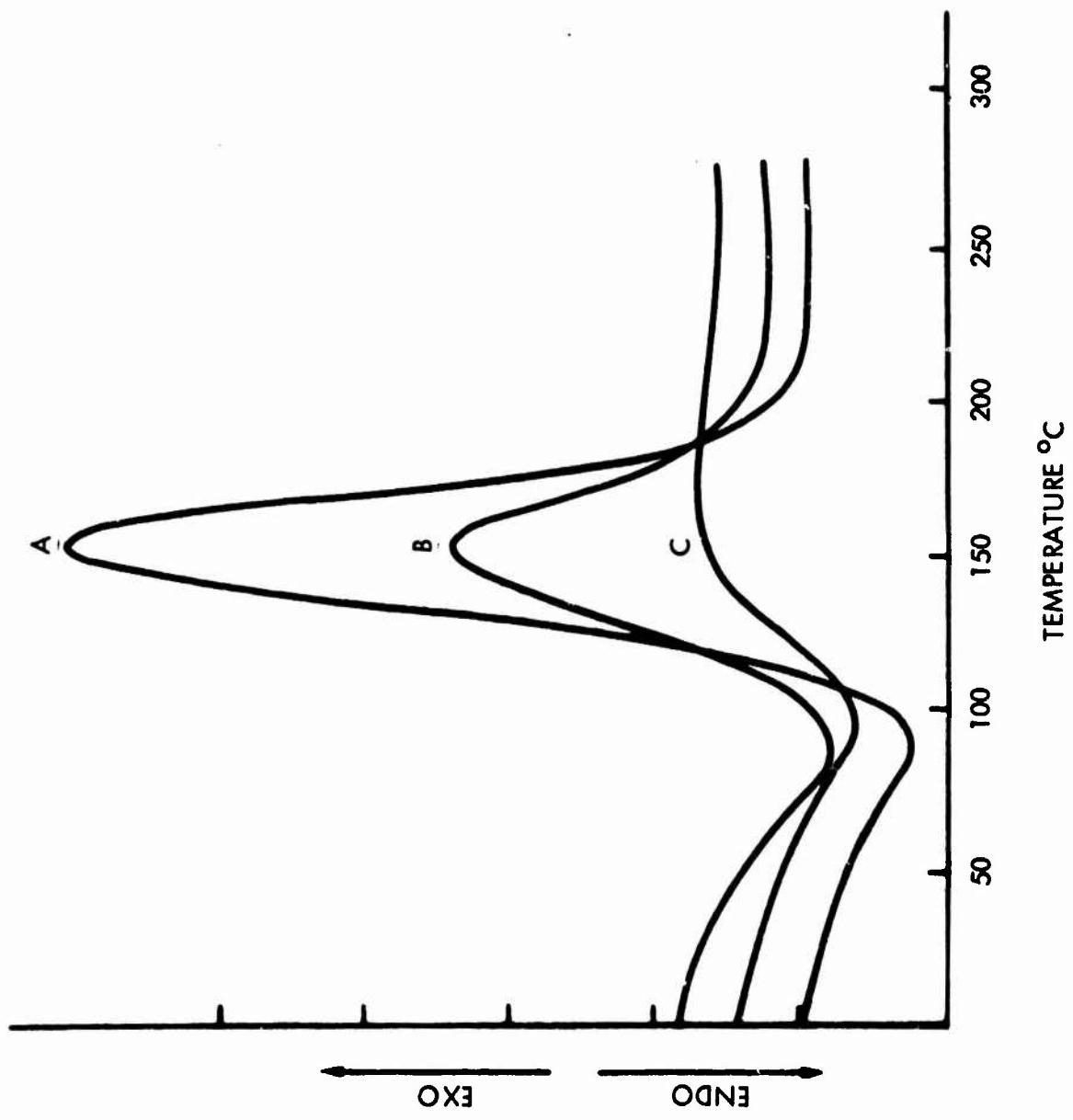


Figure 5. DSC Thermograms of DIPA-4: Measured (A) The Day After Polymerization; (B) After 6 Days; (C) After 27 Days

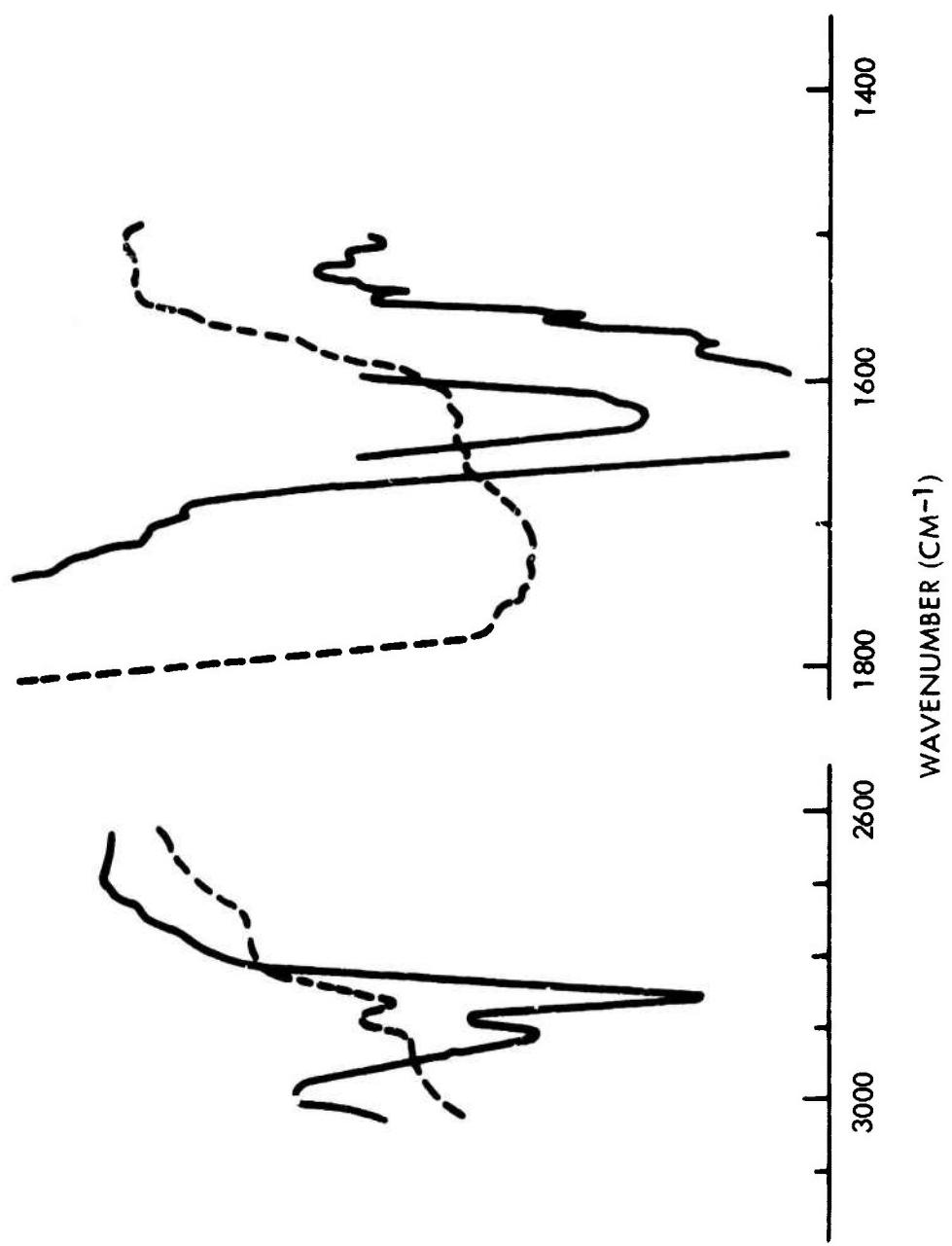


Figure 6. IR-Spectra of PDIPA Film. (—) 0 hr., (---) 42 hr.,
Unfiltered Mercury Arc Irradiation in Air

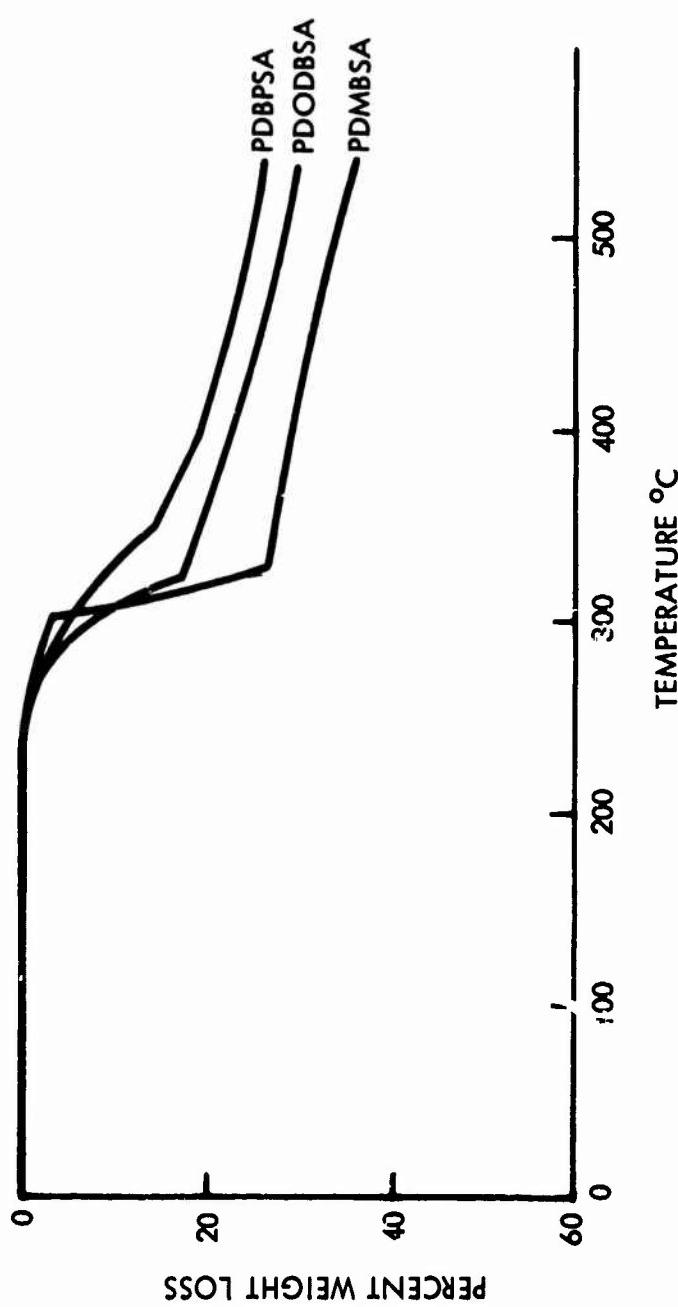


Figure 7. Thermogravimetric Analysis of Polysulfonamides

V. REFERENCES

1. Seaman, R. E., Textile Progr., 3(1), 31 (1971).
2. Lee, H., D. Stoffey, and K. Neville, Ch 6, "New Linear Polymers" McGraw Hill, 1967.
3. Wallenberger, F. T., Angew. Chem. Internat. Ed., 3(7), 460 (1964).
4. "High-Modulus Wholly Aromatic Fibers", Ed. by W. B. Black and J. Preston, Marcel & Dekker, New York, 1973.
5. Stapler, J. T., and J. Bornstein, Techn Report TR-17-CE, Nov 71, US Army Natick Laboratories.
6. Morgan, P. W., Condensation Polymers: by Interfacial and Solution Methods, Interscience Publ (1965).
7. Puffr, R., and J. Sebenda, J. Poly. Sci., c, 16, P 79 (1967).
8. Kapur, S., C. E. Rogers, and E. Baer, J. Polym. Sci., Phys. Ed., 10, p 2297 (1972).
9. Preston, J. and W. B. Black, J. Polym. Sci., c 19, p 17-27 (1967).
10. _____, Applied Polym. Sym., 9, 107 (1969).
11. Carlson, D. J., R. D. Parnell, and D. M. Wiles, J. Polym. Sci., Polymer Letters, 11, 149 (1973).
12. Perrin, D. D., W. L. E. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals", Pergamon Press (1966).
13. Hawkins, V. Lincoln, "Polymer Stabilization", Wiley-Interscience (1972).
14. Mark, H. F., N. G. Gaylord, "Encyclopedia of Polymer Science and Technology", V. 10, Interscience, p 483.
15. Kransky, J. F., and A. M. Schwartz, Nomex Ultraviolet Inhibitors, Techn Report ASD-TR-72-104, Dec 72.
16. Arnold, F. E., S. Cantor, and C. S. Marvel, J. Polym. Sci., A-1, 5, 553 (1967).
17. Evers, R. C., and G. F. L. Ehlers, J. Polym. Sci., A-1, 5, 1797 (1967).
18. Pierson, R. H., A. N. Fletcher, and E. St. C. Grantz, Anal. Chem., 28, 1213 (1956).